

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 September 2003 (18.09.2003)

PCT

(10) International Publication Number
WO 03/076511 A1

(51) International Patent Classification⁷: C08L 23/16,
23/12

TAKENOUCHI, Hiroshi [JP/JP]; 3-2-16, Tsujido,
Fujisawa-shi, Kanagawa 251-0047 (JP). **NAKAJIMA,**
Takeshi [JP/JP]; 2-42-1, Gohongi, Meguro-ku, Tokyo
153-0053 (JP).

(21) International Application Number: PCT/EP03/02518

(22) International Filing Date: 6 March 2003 (06.03.2003)

(74) Agents: **GAVERINI, Gaetano**, et al.; Basell Poliolefine
Italia S.p.A., Intellectual Property, Via Pergolesi 25,
I-20124 Milano (IT).

(25) Filing Language: English

(26) Publication Language: English

(81) Designated States (*national*): AU, BR, CA, CN, CO, CZ,
HU, ID, IL, IN, JP, KR, MX, NO, PH, PL, RO, RU, SG,
SK, UA, US, YU, ZA.

(30) Priority Data:
02075992.4 12 March 2002 (12.03.2002) EP

(84) Designated States (*regional*): European patent (AT, BE,
BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,
IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR).

(71) Applicant (*for all designated States except US*): **BASELL**
POLIOLEFINE ITALIA S.P.A. [IT/IT]; Via Pergolesi 25,
I-20124 Milano (IT).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii)) for all designations*
- *of inventorship (Rule 4.17(iv)) for US only*

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **PELLICONI,**
Anteo [IT/IT]; Via Volta, 22, I-45030 S. M. Mad-
dalena (IT). **GARAGNANI, Enea** [IT/IT]; Viale
Mons. Natale Mosconi, 76, I-44100 Ferrara (IT).
YOKOYAMA, Yutaka [JP/JP]; Estate Hachikura
103, 20-13 Daimachi, Kawasaki-ku, Kawasaki-City,
210-0814 (JP). **WASHIYAMA, Junichiro** [JP/JP];
2-27-1, Akanedai, Aoba-ku, Yokohama 227-0066 (JP).

Published:

- *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

WO 03/076511 A1

(54) Title: "POLYOLEFIN MASTERBATCH FOR PREPARING IMPACT-RESISTANT POLYOLEFIN ARTICLES"

(57) Abstract: A masterbatch composition comprising (1) 10-50 wt% of a crystalline propylene homopolymer and (2) 50-90 wt% of a blend consisting of (a) a copolymer of ethylene and one or more C4-C10 α -olefin(s), containing 10-40 of C4-C10 α -olefin(s), and (b) an amorphous copolymer of propylene and ethylene. Copolymer (b) has an ethylene content from 20-70 wt%, and an intrinsic viscosity value of the xylene-soluble moiety of from 2.2 to 3.5 dL/g, this value being equal to 0.8 to 1.2 times the intrinsic viscosity value of the xylene-soluble moiety of copolymer (a). The weight ratio of copolymers (a)/(b) is from 3/1 to 1/3. Polyolefin compositions comprising the said masterbatch composition are suitable for the manufacture of automotive parts.

“POLYOLEFIN MASTERBATCH FOR PREPARING IMPACT-RESISTANT POLYOLEFIN ARTICLES”

The present invention relates to a polyolefin masterbatch that can be used to prepare a polyolefin composition suitable for molding into relatively large articles.

Polypropylene and thermoplastic polyolefins have enjoyed wide commercial acceptance because of their outstanding cost/performance characteristics.

Polypropylene and thermoplastic polyolefins are generally injection molded into desired articles.

Polyolefin composition possessing good characteristics in terms of a balance of flexural modulus and Izod impact strength are known. Such compositions, which are described in European patent application 640649, for example, can comprise a crystalline propylene polymer, an ethylene-propylene copolymer rubber, and ethylene- C_3 - C_8 α -olefin copolymer rubber. The described compositions have, however, an unsatisfactory value of coefficient of linear thermal expansion (CLTE) and balance of values between flexural modulus and Izod impact resistance.

The polyolefin composition prepared by using the masterbatch of the present invention can be injection molded into large objects which exhibit an improved balance of mechanical properties, in particular of flexural modulus and Izod impact strength even at low temperatures (e.g. at -30°C).

In addition to the above properties, the polyolefin composition is endowed with satisfactory optical properties, in particular gloss. As required by the market, the composition of the present invention shows low gloss values.

An added advantage is that the said composition has a low value of CLTE. Said property imparts a higher dimensional stability to the final molded articles.

Thanks to the said properties, the polyolefin compositions comprising the masterbatch compositions of the present invention are, therefore, particularly suitable for the manufacture of automotive parts, in particular bumpers and side strips.

Therefore the present invention relates to a masterbatch composition comprising (percent by weight):

- 1) 10-50%, preferably 20-40%, of a crystalline propylene homopolymer; and
- 2) 50-90%, preferably 60-80% of a blend consisting of:
 - (a) a copolymer of ethylene and one or more α -olefin(s) of formula $\text{H}_2\text{C}=\text{CHR}$, where R

is a C₂-C₈ linear or branched alkyl radical, and containing 10-40, preferably 12-35% of said C₄-C₁₀ α -olefin(s) (copolymer (a)), and

- (b) an amorphous copolymer of propylene and ethylene (copolymer (b)), wherein the ethylene content is from 20-70%, preferably 30-60%, and having an intrinsic viscosity value of the xylene-soluble moiety of from 2.2 to 3.5 dL/g, this value being equal to 0.8 to 1.2 times the intrinsic viscosity value of the xylene-soluble moiety of copolymer (a);

wherein the weight ratio between copolymer (a) and copolymer (b) is from 3/1 to 1/3, preferably from 2/1 to 1/2.

The solubility in xylene is determined at ambient temperature, that is approximately 25 °C.

The method for determining the solubility in xylene is disclosed hereinafter.

From the above definitions it is evident that the term "copolymer" includes polymers containing more than two types of monomers.

The said C₄-C₁₀ alpha olefins that can be straight or branched are preferably selected from 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene and 1-octene. Particularly preferred is 1-butene.

The crystalline propylene homopolymer is generally a homopolymer soluble in xylene at ambient temperature for a percentage lower than 6% by weight, preferably lower than 4, more preferably lower than or equal to 3% by weight.

Typically, copolymer (a) has a ratio of weight average molecular weight to number average molecular weight, namely $\overline{M}_w/\overline{M}_n$, equal to or over 4. It is typically soluble in xylene at ambient temperature in a percent ranging from 30 to 80%, preferably from 40 to 70% by weight.

Typically, copolymer (b) has an ethylene content from over 35 to 60% by weight. The intrinsic viscosity value of the xylene-soluble moiety of copolymer (b) is typically from 2.4 to 3.5 dL/g.

If the value of intrinsic viscosity of copolymer (a) and/or copolymer (b) is lower than the selected values, the polyolefin masterbatch shows unwanted streaks.

Preferably the Melt Flow Rate (MFR) values for the masterbatch composition of the present invention range from 0.5 to 15 g/10 min., more preferably from 1 to 10 g /10 min.

Typically, the masterbatch of the present invention has a value of flexural modulus equal to or lower than 700 MPa, generally ranging from 100 to 500 MPa; an Izod impact value at -30 °C over 30 kJ/m²; and a value of CLTE equal to or lower than $10.5 \cdot 10^{-5} \text{ } ^\circ\text{C}^{-1}$.

The said MFR values can be obtained directly in polymerization, by properly dosing the molecular weight regulator (hydrogen), or by degradation, in particular in the presence of free radical initiators, like organic peroxides, operating with techniques well known in the art.

The polyolefin compositions prepared by mixing the masterbatch of the present invention with additional polyolefins show, as previously said, a very unique balance of properties, which is not achievable by using the masterbatch compositions of the existing art, as will be shown in the examples.

The masterbatch composition of the present invention can be prepared by a sequential polymerization, comprising at least three sequential steps, wherein components (1) and (2) are prepared in separate subsequent steps, operating in each step, except the first step, in the presence of the polymer formed and the catalyst used in the preceding step. The catalyst is only added in the first step, however its activity is such that it is still active for all the subsequent steps.

In particular, component (2) requires two sequential steps, one for preparing copolymer (a) and the other for preparing copolymer (b).

Preferably component (1) is prepared before component (2).

The order in which copolymers (a) and (b), constituting component (2), are prepared is not critical.

The polymerization, which can be continuous or batch, is carried out following known techniques and operating in liquid phase, in the presence or not of inert diluent, or in gas phase, or by mixed liquid-gas techniques. It is preferable to carry out the polymerization in gas phase.

Reaction time, pressure and temperature relative to the two steps are not critical, however it is best if the temperature is from 50 to 100 °C. The pressure can be atmospheric or higher.

The regulation of the molecular weight is carried out by using known regulators, hydrogen in particular.

Such polymerization is preferably carried out in the presence of stereospecific Ziegler-Natta catalysts. An essential component of said catalysts is a solid catalyst component comprising

a titanium compound having at least one titanium-halogen bond, and an electron-donor compound, both supported on a magnesium halide in active form. Another essential component (co-catalyst) is an organoaluminum compound, such as an aluminum alkyl compound.

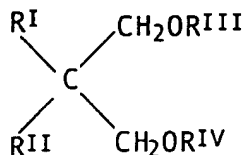
An external donor is optionally added.

The catalysts generally used in the process of the invention are capable of producing polypropylene with an isotactic index greater than 90%, preferably greater than 95%. Catalysts having the above mentioned characteristics are well known in the patent literature; particularly advantageous are the catalysts described in US patent 4,399,054 and European patent 45977.

The solid catalyst components used in said catalysts comprise, as electron-donors (internal donors), compounds selected from the group consisting of ethers, ketones, lactones, compounds containing N, P and/or S atoms, and esters of mono- and dicarboxylic acids.

Particularly suitable electron-donor compounds are phthalic acid esters, such as diisobutyl, dioctyl, diphenyl and benzylbutyl phthalate.

Other electron-donors particularly suitable are 1,3-diethers of formula:



wherein R^I and R^{II} are the same or different and are C₁-C₁₈ alkyl, C₃-C₁₈ cycloalkyl or C₇-C₁₈ aryl radicals; R^{III} and R^{IV} are the same or different and are C₁-C₄ alkyl radicals; or are the 1,3-diethers in which the carbon atom in position 2 belongs to a cyclic or polycyclic structure made up of 5, 6 or 7 carbon atoms and containing two or three unsaturations.

Ethers of this type are described in published European patent applications 361493 and 728769.

Representative examples of said diethers are 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2-isopropyl-2-isoamyl-1,3-dimethoxypropane, 9,9-bis(methoxymethyl)fluorene.

The preparation of the above mentioned catalyst components is carried out according to various methods.

For example, a $\text{MgCl}_2 \cdot n\text{ROH}$ adduct (in particular in the form of spheroidal particles) wherein n is generally from 1 to 3 and ROH is ethanol, butanol or isobutanol, is reacted with an excess of TiCl_4 containing the electron-donor compound. The reaction temperature is generally from 80 to 120 °C. The solid is then isolated and reacted once more with TiCl_4 , in the presence or absence of the electron-donor compound, after which it is separated and washed with aliquots of a hydrocarbon until all chlorine ions have disappeared.

In the solid catalyst component the titanium compound, expressed as Ti, is generally present in an amount from 0.5 to 10% by weight. The quantity of electron-donor compound which remains fixed on the solid catalyst component generally is 5 to 20% by moles with respect to the magnesium dihalide.

The titanium compounds which can be used for the preparation of the solid catalyst component are the halides and the halogen alcoholates of titanium. Titanium tetrachloride is the preferred compound.

The reactions described above result in the formation of a magnesium halide in active form. Other reactions are known in the literature, which cause the formation of magnesium halide in active form starting from magnesium compounds other than halides, such as magnesium carboxylates.

The Al-alkyl compounds used as co-catalysts comprise the Al-trialkyls, such as Al-triethyl, Al-triisobutyl, Al-tri-n-butyl, and linear or cyclic Al-alkyl compounds containing two or more Al atoms bonded to each other by way of O or N atoms, or SO_4 or SO_3 groups.

The Al-alkyl compound is generally used in such a quantity that the Al/Ti ratio be from 1 to 1000.

The electron-donor compounds that can be used as external donors include aromatic acid esters such as alkyl benzoates, and in particular silicon compounds containing at least one Si-OR bond, where R is a hydrocarbon radical.

Examples of silicon compounds are $(\text{tert-butyl})_2\text{Si}(\text{OCH}_3)_2$, $(\text{cyclohexyl})(\text{methyl})\text{Si}(\text{OCH}_3)_2$, $(\text{phenyl})_2\text{Si}(\text{OCH}_3)_2$ and $(\text{cyclopentyl})_2\text{Si}(\text{OCH}_3)_2$. 1,3-diethers having the formulae described above can also be used advantageously. If the internal donor is one of these diethers, the external donors can be omitted.

The catalysts can be pre-contacted with small amounts of olefins (prepolymerization).

Other catalysts that may be used in the process according to the present invention are metallocene-type catalysts, as described in USP 5,324,800 and EP-A-0 129 368; particularly

advantageous are bridged bis-indenyl metallocenes, for instance as described in USP 5,145,819 and EP-A-0 485 823. Another class of suitable catalysts are the so-called constrained geometry catalysts, as described in EP-A-0 416 815 (Dow), EP-A-0 420 436 (Exxon), EP-A-0 671 404, EP-A-0 643 066 and WO 91/04257. These metallocene compounds may be used in particular to produce the copolymers (a) and (b).

The masterbatch composition of the present invention can also contain additives commonly employed in the art, such as antioxidants, light stabilizers, heat stabilizers, colorants and fillers.

The masterbatch composition of the present invention can be compounded with additional polyolefins, in particular propylene polymers such as propylene homopolymers, random copolymers, and thermoplastic elastomeric polyolefin composition. Accordingly, a second embodiment of the invention relates to a thermoplastic polyolefin composition suitable for injection molding, containing the above-mentioned masterbatch compositions. Preferably, the said thermoplastic polyolefin composition comprises up to 60% by weight, typically from 10 to 45% by weight, of the masterbatch composition according the present invention.

Practical examples of the above-mentioned polyolefins are the following polymers:

- A. crystalline propylene homopolymers, in particular isotactic or mainly isotactic homopolymers;
- B. crystalline propylene copolymers with ethylene and/or a C₄-C₁₀ α -olefin, wherein the total comonomer content ranges from 0.05 to 20% by weight with respect to the weight of the copolymer. Preferred α -olefins are 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene;
- C. crystalline ethylene homopolymers and copolymers with ethylene and/or a C₄-C₁₀ α -olefin, such as HDPE;
- D. elastomeric copolymers of ethylene with propylene and/or a C₄-C₁₀ α -olefin, optionally containing minor quantities of a diene, such as butadiene, 1,4-hexadiene, 1,5-hexadiene and ethylidene-1-norbornene. The diene content is typically from 1 to 10% by weight;
- E. a thermoplastic elastomeric composition comprising a propylene homopolymer and/or one of the copolymers of item B and an elastomeric moiety comprising one or more of the copolymers of item D, typically prepared according to known methods by mixing the components in the molten state or by sequential polymerization and generally containing the said elastomeric moiety in quantities from 5 to 80% by weight.

The polyolefin composition may be manufactured by mixing the masterbatch composition and the additional polyolefin together, extruding the mixture, and pelletizing the resulting composition using known techniques and apparatus.

The polyolefin composition may also contain conventional additives such as mineral fillers, colorants and stabilizers. Mineral fillers that can be included in the composition include talc, CaCO_3 , silica, such as wollastonite (CaSiO_3), clays, diatomaceous earth, titanium oxide and zeolites. Typically the mineral filler is in particle form having an average diameter ranging from 0.1 to 5 micrometers.

The present invention also provides final articles, such as bumpers, made of the said polyolefin composition.

The particulars are given in the following examples, which are given to illustrate, without limiting, the present invention.

The following analytical methods are used to characterize the polymer compositions.

- Melt Flow Rate: ASTM method D 1238, condition L (MFR "L").
- Solubility in xylene: 2.5 g of polymer are dissolved in 250 mL of xylene at 135 °C under agitation. After 20 minutes the solution is allowed to cool to 25 °C, still under agitation, and then allowed to settle for 30 minutes. The precipitate is filtered with filter paper, the solution evaporated in nitrogen flow, and the residue dried under vacuum at 80 °C until constant weight is reached. Thus one calculates the percent by weight of polymer soluble and insoluble at room temperature (25° C).
- [η] intrinsic viscosity: determined in tetrahydronaphthalene at 135 °C.
- Ethylene and butene-1 content: I.R. Spectroscopy.
- Molecular weight (M_w and M_n): determined by the Gel Permeation Chromatography (GPC) method.
- Flexural Modulus: ISO method 178.
- Tensile strength at yield: ISO method 527.
- Tensile strength at break: ISO method 527.
- Notched IZOD impact test: ISO method 180/1A.
- VICAT: ISO method 306.
- HDT 1820 KPa: ISO method 75.
- Elongation at break and at yield: ISO method 527.
- Ductile/Brittle (D/B) transition temperature: Determined according to Basell internal

method MTM 17324, available upon request.

- Gloss: ASTM method D 2457.

- CLTE: this test method is based on ASTM methods D 696 and E831-86. Before the CLTE measurement the sample is conditioned into the TMA (thermomechanical analysis) apparatus at 120°C for 10 minutes in order to erase the stresses induced into the specimen (3.5 mm thick and 10 mm length) by injection molding. After that the dilatation curve is measured in the temperature range from 0 to 130 °C at 3 °C/min scanning rate under the probe, the load of which is 1 mN (flat probe 3.66 mm diameter).

The CLTE measurement is carried out in longitudinal way with respect to the line of injection of the polymer.

CLTE is determined as $\alpha = \Delta L / (L^0 \times \Delta T)$ in the temperature range 23-80 °C.

ΔL : length variation in the temperature range from 23 to 80 °C.

ΔT : $80 - 23 = 57$ °C

L^0 : initial specimen length.

Example 1

The solid catalyst component used in polymerization is a highly stereospecific Ziegler-Natta catalyst component supported on magnesium chloride, containing about 2.5% by weight of titanium and diisobutylphthalate as internal donor, prepared by analogy with the method described in the examples of European published patent application 674991.

CATALYST SYSTEM AND PREPOLYMERIZATION TREATMENT

Before introducing it into the polymerization reactors, the solid catalyst component described above is contacted at -5 °C for 5 minutes with aluminum triethyl (TEAL) and dicyclopentylmethoxysilane (DCPMS), in a TEAL/DCPMS weight ratio equal to about 4 and in such quantity that the TEAL/Ti molar ratio be equal to 65.

The catalyst system is then subjected to prepolymerization by maintaining it in suspension in liquid propylene at 20 °C for about 20 minutes before introducing it into the first polymerization reactor.

POLYMERIZATION

Into a first gas phase polymerization reactor a polypropylene homopolymer (component 1) is produced by feeding in a continuous and constant flow the prepolymerized catalyst system, hydrogen (used as molecular weight regulator) and propylene in the gas state.

Polymerization conditions are shown in Table 1.

The polypropylene homopolymer produced in the first reactor is discharged in a continuous flow and, after having been purged of unreacted monomers, is introduced, in a continuous flow, into a second gas phase reactor, together with quantitatively constant flows of hydrogen, propylene and ethylene in the gas state.

In the second reactor a propylene-ethylene copolymer (copolymer (b) belonging to component (2) is produced. Polymerization conditions, molar ratio of the reactants and composition of the copolymers obtained are shown in Table 1.

The polymer coming from the second reactor is discharged in a continuous flow and, after having been purged of unreacted monomers, is introduced, in a continuous flow, into a third gas phase reactor, together with quantitatively constant flows of hydrogen, ethylene and 1-butene in the gas state.

In the third reactor an ethylene-butene-1 copolymer (copolymer (a) belonging to component (2) is produced. Polymerization conditions, molar ratio of the reactants and composition of the copolymers obtained are shown in Table 1.

The polymer particles exiting the third reactor are subjected to a steam treatment to remove the reactive monomers and volatile substances, and then dried.

Then the polymer particles are introduced in a rotating drum, where they are mixed with 0.05% by weight of paraffin oil ROL/OB 30 (having a density of 0.842 kg/L at 20 °C according to ASTM method D 1298 and flowing point of -10 °C according to ASTM method D 97), 0.15% by weight of Irganox® B 215 (made of about 34% Irganox® 1010 and 66% Irgafos® 168) and 0.05% by weight of calcium stearate.

Then the polymer particles are introduced in a twin screw extruder Berstorff ZE 25 (length/diameter ratio of screws: 33) and extruded under nitrogen atmosphere in the following conditions:

Rotation speed:	250 rpm;
Extruder output:	6-20 kg/hour;
Melt temperature:	200-250 °C.

The characteristics relating to this polymer composition, reported in Table 2, are obtained from measurements carried out on the so extruded polymer.

This masterbatch is able to give the same or even better characteristics than the two commercial high impact masterbatches did as well as a lower value of CLTE that gives a higher dimensional stability to the final molded articles.

A masterbatch only based on an ethylene-butene-1 copolymer as elastomeric moiety doesn't succeed in lowering so much the CLTE.

Examples 2 and 3

Example 1 is repeated. The polymerization conditions, molar ratio of the reactants and composition of the copolymers obtained are shown in Table 1.

The characteristics relating to these polymer compositions, reported in Table 2, are obtained from measurements carried out on the so extruded polymers.

Examples 4-6 and Comparative Examples 1-5

The masterbatches of examples 1-3 are evaluated in blend with additional polyolefins and mineral fillers in comparison with blends comprising known masterbatches. The latter have the following compositions:

- Masterbatch A consisting of
 - 44.2 wt% of a propylene homopolymer with MFR "L" of 90 g/10 min, and
 - 55.8 wt% of an ethylene/propylene copolymer containing 49 wt% of ethylene and having an intrinsic viscosity of the moiety soluble in xylene of 3.35 dL/g.

The whole composition has an MFR "L" value of 2.7 g/10 min and a flexural modulus value of 400 MPa.

- Masterbatch B consisting of
 - 30 wt% of a propylene homopolymer with MFR "L" of 140 g/10 min;
 - 30 wt% of an ethylene/propylene copolymer containing 34 wt% of ethylene and having an intrinsic viscosity of the moiety soluble in xylene of 2.45 dL/g; and
 - 40 wt% of an ethylene/propylene copolymer containing 70 wt% of ethylene and having an intrinsic viscosity of the moiety soluble in xylene of 2.95 dL/g.

The whole composition has an MFR "L" value of 2.8 g/10 min, an intrinsic viscosity of the moiety soluble in xylene of 2.7 dL/g and a flexural modulus value of 400 MPa.

- Mastrebatch C consisting of
 - 18 wt% of a propylene homopolymer with MFR "L" of 105 g/10 min, and
 - 82 wt% of an ethylene/butene-1 copolymer containing 75 wt% of ethylene and having an intrinsic viscosity of the moiety soluble in xylene of 2.40 dL/g.

The whole composition has an MFR "L" value of 0.6 g/10 min and a flexural modulus value of 150 MPa.

The additional polymers used in the examples and comparative examples are as follows:

- Polymer I consisting of
 - 83 wt% of a propylene homopolymer with MFR "L" of 22 g/10 min, and
 - 17 wt% of an ethylene/propylene copolymer containing 50 wt% of ethylene and having an intrinsic viscosity of the moiety soluble in xylene of 2.7 dL/g.

The whole composition has an MFR "L" value of 12 g/10 min and a flexural modulus value of 1450 MPa.
- Polymer II consisting of
 - 84 wt% of a propylene homopolymer with MFR "L" of 86 g/10 min, and
 - 16 wt% of an ethylene/propylene copolymer containing 50 wt% of ethylene and having an intrinsic viscosity of the moiety soluble in xylene of 2.25 dL/g.

The whole composition has an MFR "L" value of 43 g/10 min and a flexural modulus value of 1450 MPa.
- Polymer III consisting of
 - 91 wt% of a propylene homopolymer with MFR "L" of 134 g/10 min, and
 - 9 wt% of an ethylene/propylene copolymer containing 55 wt% of ethylene and having an intrinsic viscosity of the moiety soluble in xylene of 1.5 dL/g.

The whole composition has an MFR "L" value of 100 g/10 min and a flexural modulus value of 1500 MPa.
- Polymer IV consisting of
 - 87 wt% of a propylene homopolymer with MFR "L" of 180 g/10 min, and
 - 13 wt% of an ethylene/propylene copolymer containing 60 wt% of ethylene and having an intrinsic viscosity of the moiety soluble in xylene of 1.5 dL/g.

The whole composition has an MFR "L" value of 100 g/10 min and a flexural modulus value of 1500 MPa.

The results of the comparison, reported in Tables 3 and 4, point out the promising properties imparted by the masterbatches according to the present invention to the compounds.

Table 4 reports a comparison between a masterbatch only based on a ethylene/butene-1 rubber and a commercial masterbatch in blends similar to the ones reported in table 3. In the comparative compounds no advantage in terms of CLTE and mechanical characteristics have been obtained.

The masterbatches according to the present invention are able to give the same or even better characteristics than the commercial high impact masterbatch did as well as a lower value of CLTE that gives a higher dimensional stability to the final molded articles.

Table 1

	Units	Examples		
		1	2	3
TEA/donor weight ratio		10	4.7	4.8
TEA/catalyst weight ratio		10	4.9	4.8
1° Reactor (Homopolypropylene)				
Split	wt%	36	36	34
Temperature	°C	80	70	70
Pressure	MPa	2.0	1.6	1.6
H ₂ /C ₃ ⁻	mol	0.08	0.12	0.13
MFR "L"	g/10 min	82.5	74.5	79.0
Total Xylene Soluble (X.S.)	wt%	2.2	1.9	2.2
Bulk poured density	g/cc	0.30	0.31	0.30
2° Reactor (Ethylene-propylene copolymer rubber, EPR)				
Split	wt%	34	35	37
Temperature	°C	65	60	60
Pressure	MPa	1.8	1.8	1.8
H ₂ /C ₃ ⁻	mol	0.07	0.08	0.07
H ₂ /C ₂ ⁻	mol	0.10	0.17	0.24
C ₂ ⁻ /(C ₂ ⁻ + C ₃ ⁻)	mol	0.32	0.32	0.22
Ethylene in EPR	wt%	45	46	36
Xylene soluble of EPR	wt%	87	86	90
MFR "L"	g/10 min	7.9	7.2	6.1
Total xylene soluble	wt%	43.2	43.3	47.6
Ethylene content	wt%	21.8	22.6	18.8
X.S. I.V.	dL/g	2.91	2.85	2.65
3° Reactor (Ethylene-butene-1 copolymer rubber, EBR)				
Temperature	°C	70	70	70
Pressure	MPa	1.4	1.4	1.4
Split	wt%	30	29	29
H ₂ ⁻ /C ₂ ⁻	mol	0.22	0.22	0.21
C ₄ ⁻ /(C ₂ ⁻ + C ₄ ⁻)	mol	0.48	0.48	0.48
Butene-1 in EBR	wt%	25	25	25
Xylene soluble of EBR	wt%	-	46	49
X.S. I.V. of EBR	dL/g	2.6	2.65	2.89

Total Composition				
MFR "L"	g/10 min	4.0	2.3	2.8
Total xylene soluble	wt%	44.3	44.0	48.0
Ethylene content	wt%	37.9	37.9	35.3
Butene-1 content	wt%	7.6	7.2	7.2
I.V. _{EPR} /I.V. _{EBR} ratio		1.12	1.07	0.92
X.S. I.V.	dL/g	2.81	2.79	2.72

Table 2

Properties	Units	Examples		
		1	2	3
MFR "L"	g/10 min	4.0	2.3	2.8
Flexural modulus	MPa	390	255	220
Tensile strength at yield	MPa	9.3	7.6	7.5
Elongation at yield	%	33.4	36.5	60.0
Tensile strength at break	MPa	13.1	11.1	10.0
Elongation at break	%	460	415	330
Izod at -40 °C	kJ/m ²	N.B.	N.B.	N.B.
Izod at -50 °C	kJ/m ²	80% N.B.	N.B.	N.B.
Gloss 60° on 1 mm thick plaque	%	51.2	88.2	86.2
Longitudinal shrinkage	%	-	0.54	0.68
Transversal shrinkage	%	-	0.58	0.70
Longitudinal CLTE	°C ⁻¹ × 10 ⁻⁵	8.8	8.7	10.1

N.B.: not broken

Table 3

Components and properties	Comparative examples		Examples		
	2	3	4	5	6
Masterbatch A wt%	47.00	-	-	-	-
Masterbatch B wt%	-	34.00	-	-	-
Masterbatch of example 1 wt%	-	-	38.5	-	-
Masterbatch of example 2 wt%	-	-	-	38.50	-
Masterbatch of example 3 wt%	-	-	-	-	37.30
Polymer I wt%	-	20.00	29.87	19.87	21.57
Polymer II wt%	13.50	20.00	5.50	15.5	15.00
Polymer IV wt%	13.50	-	-	-	-
Talc IMI HM-05® wt%	22.00	22.00	22.00	22.00	22.00
Additives wt%	4.00	4.00	4.13	4.13	4.13

MFR "L" g/10 min	6.0	5.9	5.3	5.7	6.1
Flexural modulus MPa	1592	1538	1657	1610	1610
Tensile strength at yield MPa	15.1	16.2	17.2	16.1	16.0
Elongation at yield %	3.0	-	-	4.6	4.6
Tensile strength at break MPa	12.2	12.6	13.6	12.7	13.6
Elongation at break %	42	129	91	120	340
Vicat 5 kg °C	41.0	-	-	45.9	48.1
HDT 1820 kPa °C	52	-	-	50	53
Izod at 23 °C kJ/m ²	48.4 N.B.	49.3 N.B.	54.0 N.B.	55.3 N.B.	54.4 N.B.
Izod at 0 °C kJ/m ²	29.6	37.7 N.B.	38.5 N.B.	45.6 N.B.	41.2 N.B.
Izod at -20 °C kJ/m ²	10.4	8.7	9.6	14.8	10.3
Izod at -30 °C kJ/m ²	9.3	-	-	8.9	7.1
D/B transition temperature °C	-49	-45.9	<-50.0	-55	-49
Gloss 60° on plaque %	13.2	20.5	17.1	25.1	33.8
Longitudinal CLTE °C ⁻¹ x10 ⁻⁵	8.7	8.1	6.6	7.3	8.4
Longitudinal shrinkage %	0.82	-	-	0.69	0.76
Transversal shrinkage %	1.00	-	-	0.88	0.93

Total rubber wt%	30.6	30.6	30.6	30.6	30.8
Rubber coming from masterbatch wt%	26.3	23.8	24.6	24.6	24.6

Table 4

Components and properties	Units	Comparative examples	
		4	5
Masterbatch C	wt%	37.00	--
Masterbatch B	wt%	--	37.00
Polymer II	wt%	13.93	25.93
Polymer III	wt%	23.00	--
Polymer I	wt%	--	11.00
Talc IMI HM-05®	wt%	22.00	22.00
Additives	wt%	4.07	4.07

MFR "L"	g/10 min	4.0	5.3
Flexural modulus	MPa	1380	1360
Tensile strength at yield	MPa	15.8	14.8
Elongation at yield	%	9.7	7.2
Tensile strength at break	MPa	17.2	12.4
Elongation at break	%	490	365
VICAT 5 kg	°C	43	39
HDT 1820 kPa	°C	49	48
Hardness Rockwell	R	19	14
Izod at 23 °C	kJ/m ²	65.0 N.B.	60.1 N.B.
Izod at 0 °C	kJ/m ²	60.2 N.B.	57.4 N.B.
Izod at -20 °C	kJ/m ²	37.9	38.3
D/B transition temperature	°C	<-60	<-60
Gloss 60° (1 mm thick plaque)	%	23.0	34.0
Longitudinal CLTE	°C ⁻¹ x 10 ⁻⁵	5.8	6.2

Total rubber	wt%	34.0	32.2
Rubber coming from masterbatch	wt%	29.6	25.9

CLAIMS

1. A masterbatch composition comprising (percentage by weight):
 - 1) 10-50%, preferably 20-40%, of a crystalline propylene homopolymer;
 - 2) 50-90%, preferably 60-80% of a blend consisting of:
 - a) a copolymer of ethylene and one or more α -olefin(s) of formula $H_2C=CHR$, where R is a C_2 - C_8 linear or branched alkyl radical, and containing 10-40, preferably 12-35% of said C_4 - C_{10} α -olefin(s) (copolymer (a)), and
 - b) an amorphous copolymer of propylene and ethylene (copolymer (b)), wherein the ethylene content is from 20-70%, and having an intrinsic viscosity value of the xylene-soluble moiety of from 2.2 to 3.5 dL/g, this value being equal to 0.8 to 1.2 times the intrinsic viscosity value of the xylene-soluble moiety of copolymer (a);wherein the weight ratio between copolymer (a) and copolymer (b) is from 3/1 to 1/3.
2. The masterbatch composition of claim 1, wherein copolymer (b) has an ethylene content from over 30 to 60% by weight.
3. The masterbatch composition of claim 1, wherein the weight ratio (a)/(b) is from 2/1 to 1/2.
4. A thermoplastic polyolefin composition containing the masterbatch compositions according to claims 1-3.
5. The polyolefin composition of claim 4 wherein the content of the masterbatch composition is up to 60% by weight.
6. The polyolefin composition of claim 4 wherein the masterbatch composition is blended with additional polyolefins.
7. The polyolefin composition of claim 6 wherein the propylene polymer is selected from propylene homopolymers, random copolymers, and heterophasic copolymers composition.
8. The polyolefin composition of claim 4 also comprising a mineral filler.
9. Bumpers comprising the masterbatch composition of claim 1.
10. A process for preparing the masterbatch composition of claim 1 by a sequential polymerization, comprising at least three sequential steps, wherein components (1) and (2) are prepared in separate subsequent steps, operating in each step, except the first step, in the presence of the polymer formed and the catalyst used in the preceding step.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 03/02518

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L23/16 C08L23/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 704 463 A (MITSUI PETROCHEMICAL IND) 3 April 1996 (1996-04-03) example 3	1-10
X	EP 0 884 353 A (ADVANCED ELASTOMER SYSTEMS ; EXXON CHEMICAL PATENTS INC (US)) 16 December 1998 (1998-12-16) tables 1,2	1-10
A	EP 0 832 925 A (MONTELL NORTH AMERICA INC) 1 April 1998 (1998-04-01) table 1	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

16 June 2003

Date of mailing of the international search report

25/06/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Schmidt, H

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 03/02518

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0704463	A	03-04-1996	DE 69511023 D1	02-09-1999
			DE 69511023 T2	27-01-2000
			EP 0704463 A1	03-04-1996
			US 5753769 A	19-05-1998
			CA 2157399 A1	12-10-1995
			CN 1130915 A ,B	11-09-1996
			DE 69518094 D1	24-08-2000
			DE 69518094 T2	22-03-2001
			EP 0816395 A2	07-01-1998
			WO 9527741 A1	19-10-1995
			US 5969049 A	19-10-1999
EP 0884353	A	16-12-1998	EP 0884353 A1	16-12-1998
			DE 69716717 D1	05-12-2002
			JP 11060847 A	05-03-1999
EP 0832925	A	01-04-1998	US 6048942 A	11-04-2000
			AT 202588 T	15-07-2001
			AU 721480 B2	06-07-2000
			AU 3931097 A	02-04-1998
			BR 9704929 A	01-09-1998
			CA 2217165 A1	30-03-1998
			CN 1185458 A	24-06-1998
			DE 69705373 D1	02-08-2001
			DE 69705373 T2	15-11-2001
			EP 0832925 A1	01-04-1998
			ES 2158417 T3	01-09-2001
			JP 11001585 A	06-01-1999
			PL 322371 A1	14-04-1998
			RU 2194726 C2	20-12-2002
			SK 131297 A3	10-03-1999
			TR 9701086 A2	21-04-1998